COMMUNICATION

A highly asymmetric, Lewis acid-catalysed Diels–Alder reaction using optically active 2-(3-tolyl-*p*-sulfinyl)furyl α,β-unsaturated ketones as a dienophile

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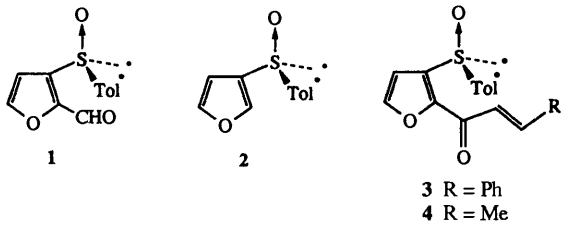
The Diels–Alder reaction of chiral 2-(3-tolyl-*p*-sulfinyl)furyl α,β-unsaturated ketones 3 and 4 with cyclopentadiene in the presence of a Lewis acid proceeds smoothly to give the corresponding *endo* adducts 5a and 6a, respectively, in excellent yield with high diastereoselectivity.

The asymmetric Diels–Alder reaction is one of the most useful reactions in organic synthesis.[1] To effect high levels of stereocontrol, the use of chiral dienophiles, chiral dienes, or chiral Lewis acids has been reported.[2] Most studies on the reactions using chiral sulfoxides as a sulfinyl dienophile have dealt with α-sulfinylacrylate derivatives, whose sulfinyl oxygen should coordinate tightly with a Lewis acid and the carbonyl oxygen, resulting in the favourable formation of a conformationally rigid six-membered chelate.[3] However, little work has been done on the asymmetric Diels–Alder reactions of dienophiles that possess a reaction site which may be remote from the sulfinyl group, *e.g.* β′-sulfinyl α,β-unsaturated enones. Recently we reported the asymmetric allylation of (*S*)-3-tolyl-*p*-sulfinyl-2-furaldehyde **1**, prepared from sulfinylfuran **2**,[4] in which the



sulfinyl substituent is in the β-position with respect to the carbonyl group.

As part of our studies on asymmetric additions using chiral sulfoxides whose sulfinyl group is remote from the reactive site,[4,5] we were intrigued by the use of a chiral sulfinylfuryl enone as a dienophile. Here we report the highly diastereoselective Diels–Alder reactions of sulfoxides **3** and **4** with cyclopentadiene in the presence of catalytic amounts of a Lewis acid.

The dienophiles **3** and **4** were prepared by a two-step reaction sequence in good yield: (i) the lithiation of **2**[4,6] followed by addition to *trans*-cinnamaldehyde or crotonaldehyde (*trans*-but-2-enal), and (ii) MnO_2 oxidation of the resulting secondary alcohols.

All reactions were carried out with **3** and **4** and cyclopentadiene (30 equiv.) in the absence or presence of a Lewis acid (Table 1). Attempts to employ ZnX_2 in the reactions or to conduct the reactions without a Lewis acid were unsuccessful, resulting in the production of nearly 1 : 1 mixtures of both the *endo* and the *exo* adducts (*cf.* entry 1). Although the reaction involving the use of $TiCl_4$ as a Lewis acid[7] at −20 °C was sluggish (entry 2), treatment of **3** and cyclopentadiene with

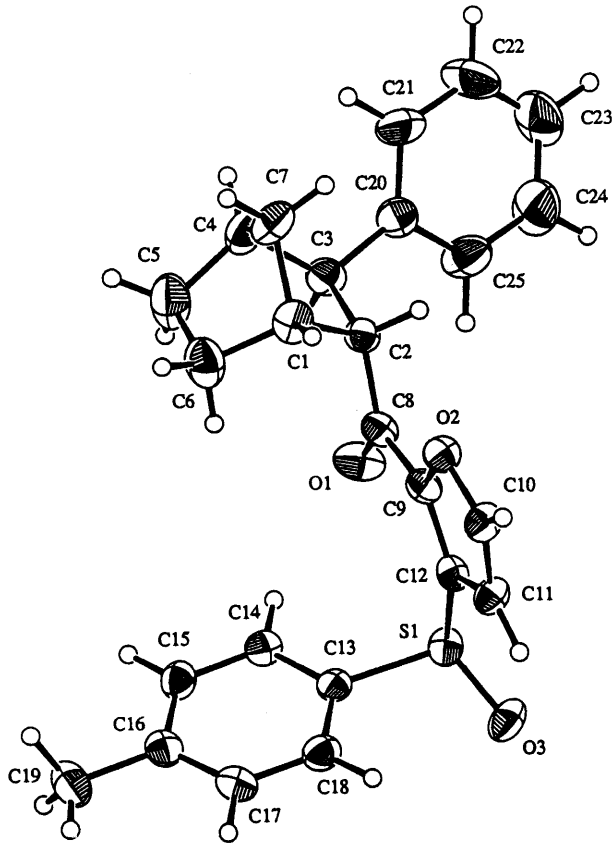
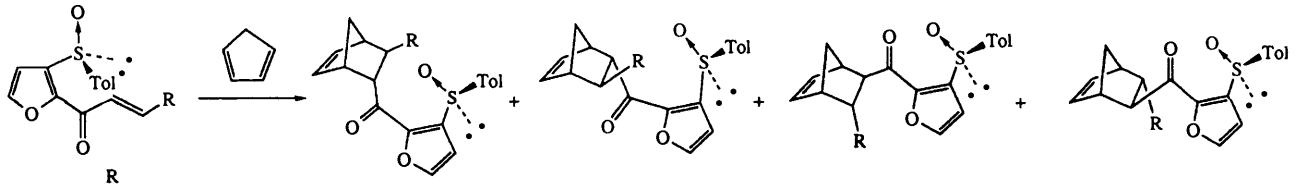


Fig. 1 ORTEP drawing of the structure of compound **7** with crystallographic numbering scheme (hydrogen atoms omitted)

1.0 equiv. of BF_3·Et_2O afforded the adducts **5** in a ratio of 65 : 32 : 2 : 1 in quantitative yield (entry 3). Of all the Lewis acids used in stoichiometric amounts that have been screened, $AlCl_3$ effected the highest diastereoselectivities (entries 4 and 5).

To make the Diels–Alder reaction practically useful, the amount of the Lewis acid should be reduced to a catalytic amount. From this viewpoint, $AlCl_3$ was examined first. When the reaction was carried out with 0.2 equiv. of $AlCl_3$ at 25 °C, a high level of diastereoselectivity was achieved (entry 6), whilst the reaction conducted at lower temperature gave unsatisfactory results. On the other hand, the lanthanoid triflate-promoted Diels–Alder reactions[8] proceeded smoothly at room temperature to give adducts with both high *endo* stereoselectivity [(**a** + **b**) *vs.* (**c** + **d**)] and high *endo* diastereoselectivity (**a** *vs.* **b**), in excellent yields. Adducts **5** obtained were inseparable from each other by column chromatography, but were separated with the aid of HPLC. These diastereoselective Diels–Alder reactions of **3** (*i.e.* entry 6), however, led to the isolation of the major *endo* adduct **5a** by recrystallisation from the original mixture of the adducts.

Table 1 Asymmetric Diels–Alder reaction of sulfinyl dienophile **3** and **4** with cyclopentadiene

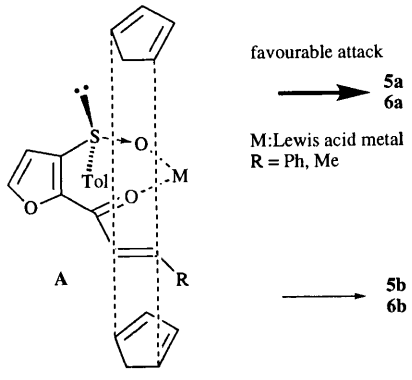


3 R = Ph
4 R = Me

5a **6a** **5b** **6b** **5c** **6c** **5d** **6d**

Entry	R	Lewis acid	Equiv.	Reaction conditions: Solvent	Time (*t*/h)	Temp. (*T*/°C)	Product ratio[a] a:b:c:d	Ratio, *endo*/*exo* (a + b)/(c + d)	De (%) *endo*	Isolated total yield (%)
1	Ph	none		benzene	7	80	27:36:17:20	63/37	−14[b]	72
2	Ph	$TiCl_4$	1.0	CH_2Cl_2	16	−20	—	—	—	0
3	Ph	$BF_3{\cdot}Et_2O$	1.0	CH_2Cl_2	20	−20	65:32:2:1	97/3	34	100
4	Ph	$AlCl_3$	1.0	CH_2Cl_2	3	−20	94:2:4: ~0	96/~4	97	100
5	Me	$AlCl_3$	1.0	CH_2Cl_2	3	25	89:3:7:1	92/8	93	95
6	Ph	$AlCl_3$	0.2	CH_2Cl_2	16	25	88:4:7:1	92/8	91	100
7	Ph	$Yb(OTf)_3$	1.0	CH_2Cl_2	3	25	84:10:4:2	94/6	78	96
8	Ph	$Yb(OTf)_3$	0.2	THF	20	25	71:10:13:6	81/19	75	39
9	Ph	$Yb(OTf)_3$	0.2	toluene	20	25	53:21:17:9	74/26	44	64
10	Ph	$Yb(OTf)_3$	0.2	CH_2Cl_2	20	25	83:6:9:2	89/11	87	88
11	Ph	$Nd(OTf)_3$	0.2	CH_2Cl_2	18	25	88:4:7:1	92/8	92	100
12	Ph	$Sm(OTf)_3$	0.2	CH_2Cl_2	19	25	89:3:6:2	92/8	93	100
13	Me	$AlCl_3$	0.2	CH_2Cl_2	24	25	74:16:8:2	90/10	64	87
14	Me	$Yb(OTf)_3$	0.2	CH_2Cl_2	20	25	87:4:7:2	91/9	91	94
15	Me	$Nd(OTf)_3$	0.2	CH_2Cl_2	20	25	89:5:5:1	94/6	89	100
16	Me	$Sm(OTf)_3$	0.2	CH_2Cl_2	20	25	90:4:5:1	94/6	91	97

[a] Ratios of the adducts **5** determined by HPLC analysis. Ratios of **6a** and **6b** estimated by integration of the pertinent olefinic signals in the ^1H NMR spectrum because of insufficient separation by HPLC. Ratios of **6c** and **6d** determined by HPLC analysis. [b] The negative sign indicates that the adduct **5b** in excess is diastereoisomeric to the adduct **5a**.



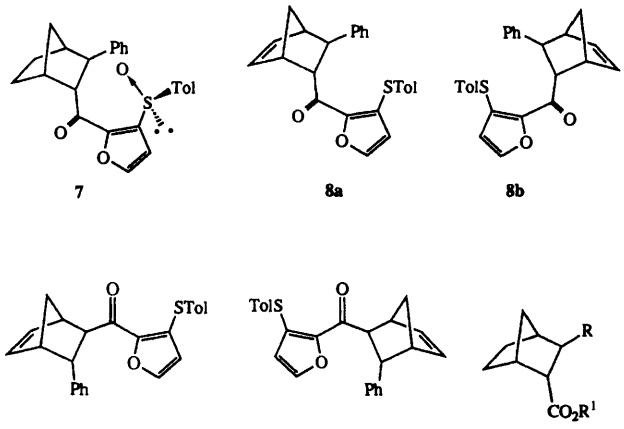


Fig. 2 Mechanism of asymmetric Diels–Alder reaction

The absolute stereochemistry of **5a** was established by X-ray crystal analysis of a suitable crystal of product **7**, obtained by hydrogenation of the 4,5-double bond of **5a** (Fig. 1). The stereochemistry of the other *endo* diastereoisomer **5b** was confirmed by the following reaction sequence. Reduction of **5a** with Zn–$TiCl_4$[9] afforded the corresponding sulfide **8a**, which was again transformed into the sulfoxides **5a** and the enantiomer of **5b** in a ratio of 1:1 by oxidation with *m*-chloroperoxybenzoic acid. Since the mixture was separable by HPLC, the *endo* configuration could be ascertained for **5b**. For a sample for HPLC analysis, all four possible isomers were also obtained by Zn–$TiCl_4$ reduction of the original mixture of **5a–d** followed by oxidation of the resulting sulfides **8** and **9**. Both the *endo* isomers and the *exo* isomers obtained by this oxidation showed nearly equal peak intensities on the HPLC analysis. The stereochemistry of the adducts **5c** and **5d** was tentatively assigned on the basis of the reaction mechanism previously proposed.[3] In a similar manner to the sequence for **5**, the stereochemistry of the adducts **6** derived from the Diels–Alder reaction of **4** was assigned. The stereochemical course of the highly diastereoselective Diels–Alder reaction using sulfinyl dienophiles **3** and **4** is not clear at present, but would be consistent with the previous proposal.[3] Since the cyclic transition state **A** would be favoured under the chelation-controlled conditions, in *endo* mode the addition of cyclopentadiene might take place not from the sterically hindered *p*-tolyl group, but from the less hindered lone-paired electrons site, giving the major *endo* adduct **5a** or **6a** (Fig. 2).

Although numerous efforts to access chiral bicyclo[2.2.1]-heptene and -heptane systems *via* asymmetric Diels–Alder reactions have been reported, little attention has been paid to the elucidation of absolute configuration of such a simple system as **10**[10] except for a related system **11**.[11] We have devised a facile entry to (1*R*)-3-*exo*-phenylbicyclo-[2.2.1]heptane-2-*endo*-carboxylic acid **10** through oxidative

degradation of the furan moiety in **7**. Treatment of **7** with RuO_4, prepared from $RuCl_3$ and $NaIO_4$ in a CCl_4–H_2O–MeCN solvent system,[12] gave the acid (−)-**10** which was further transformed into the corresponding ester (−)-**12**. Similarly the adduct **6a** was transformed into the known compound (−)-**11**.†

Experimental‡

(S_S)-*trans*-2-Cinnamoyl-3-(tolyl-*p*-sulfinyl)furan 3§

To a solution of diisopropylamine (0.20 cm^3, 1.46 mmol) in tetrahydrofuran (THF) (12 cm^3) at 0 °C was added dropwise butyllithium (1.68 mol dm^{-3} in hexane; 0.87 cm^3, 1.46 mmol) under argon. After being stirred for 1 h, the mixture was cooled to −78 °C and sulfinyl furan **2** (250 mg, 1.21 mmol) in THF (3 cm^3) was added. After stirring for 1 h, *trans*-cinnamaldehyde (0.31 cm^3, 2.42 mmol) in THF (5 cm^3) was added. The mixture was stirred for 11 h at −78 °C. After the mixture was treated with saturated aq. NH_4Cl (100 cm^3), the aqueous phase was extracted with AcOEt (3 × 30 cm^3). The combined organic phases were washed with saturated brine (50 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue (734 mg) was purified by column chromatography on silica with hexane–AcOEt (1:1) as the eluent to afford the cinnamyl alcohol as a 1:1 diastereoisomeric mixture (400 mg, 98%).

Without further purification, a mixture of the alcohol (400 mg, 1.18 mmol) and MnO_2 (2.5 g) in chloroform (20 cm^3) was stirred vigorously at room temperature for 0.5 h. After filtration with the aid of a short pad of Celite, the solid filter was washed with chloroform (30 cm^3). The combined washings and filtrate were concentrated under reduced pressure to give **3** (342 mg, 86%) as a pale yellow solid, mp 149–150 °C (Found: C, 71.2; H, 4.8. $C_{20}H_{16}O_3S$ requires C, 71.4; H, 4.8%); $[\alpha]_D^{24}$ −771.8 (*c* 1, $CHCl_3$); *m/z* 336 (M^+), 320, 287, 229, 217, 201 and 103; $\nu_{max}(CHCl_3)/cm^{-1}$ 1645, 1590, 1465, 1365, 1325, 1130 and 965; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.36 (3 H, s), 7.14 (1 H, d, *J* 1.6), 7.26 (2 H, d, *J* 8.1), 7.48 (1 H, d, *J* 16.1), 7.4–7.5 (3 H, m), 7.61 (1 H, d, *J* 1.6), 7.6–7.7 (2 H, m), 7.80 (2 H, d, *J* 8.1) and 7.89 (1 H, d, *J* 16.1).

Typical procedure for the Diels–Alder reaction with cyclopentadiene

To a solution of **3** (1.50 g, 4.46 mmol) and $AlCl_3$ (595 mg, 4.46 mmol) in dichloromethane (60 cm^3) at −20 °C was added in one portion cyclopentadiene (9.2 cm^3, 111 mmol). After being stirred for 3 h at −20 °C, the mixture was treated with saturated aq. NH_4Cl (40 cm^3). The aqueous layer was extracted with chloroform (50 cm^3) and the combined organic extracts were washed with saturated brine (100 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography on silica. Elution with hexane gave a cyclopentadiene dimer. Further elution with hexane–AcOEt (9:1→1:1) afforded a mixture of the adducts **5** (1.79 g, 100%) in the ratio of 94:2:4: ~0. In this case no *exo* minor adduct **5d** could be detected by HPLC and ^1H NMR analysis. The major adduct, (1*S*,2*R*,3*R*,S_S)-3′-(tolyl-*p*-sulfinyl)-2′-furoyl-3-phenylbicyclo[2.2.1]hept-5-ene **5a** was isolated in pure form after recrystallisation of the original mixture from hexane–Et_2O, mp 116–118 °C (Found: C, 74.6; H, 5.5. $C_{25}H_{22}O_3S$ requires C, 74.6; H, 5.5%); $[\alpha]_D^{26}$ −541 (*c* 1, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1665, 1555, 1470, 1375, 1265, 1075 and 1040; δ_H(270 MHz; $CDCl_3$; Me_4Si) 1.58 (1 H, dd, *J* 8.7 and 1.7), 1.95 (1 H, d, *J* 8.7), 2.37 (3 H, s), 3.06 (1 H, br s), 3.37 (2 H, br), 3.80 (1 H, dd, *J* 5.1 and 3.4), 5.48 (1 H, dd, *J* 5.6 and 2.7), 6.41 (1 H, dd, *J* 5.6 and 3.2), 7.05 (1 H, d, *J* 1.8), 7.18–7.30 (7 H, m), 7.49 (1 H, d, *J* 1.8) and 7.70 (2 H, d, *J* 8.3). Minor *endo* isomer **5b** was isolated by HPLC of the mother liquor fraction separated from **5a** after recrystallisation of the crude product, mp 97–99 °C; $[\alpha]_D^{19}$ −183 (*c* 0.4, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1670, 1560, 1480, 1380, 1270, 1080 and 1045; δ_H(270 MHz; $CDCl_3$; Me_4Si) 1.65 (1 H, dd, *J* 8.6 and 1.7), 1.97 (1 H, d, *J* 8.6), 2.35 (3 H, s), 3.07 (1 H, br s), 3.38 (1 H, br d, *J* 3.5), 3.49 (1 H, br s), 3.75 (1 H, dd, *J* 5.0 and 3.5), 5.94 (1 H, dd, *J* 5.6 and 2.8), 6.51 (1 H, dd, *J* 5.6 and 2.9), 7.08 (1 H, d, *J* 1.7), 7.1–7.8 (5 H, m), 7.17 (2 H, d, *J* 8.3), 7.52 (1 H, d, *J* 1.7) and 7.74 (2 H, d, *J* 8.3). **5c**: δ_H(270 MHz; $CDCl_3$; Me_4Si) 1.52 (1 H, dd, *J* 8.8 and 1.5), 1.73 (1 H, d, *J* 8.8), 2.35 (3 H, s), 3.02 (1 H, br s), 3.16 (1 H, br s), 3.35 (1 H, br d, *J* 5.4), 3.89 (1 H, dd, *J* 5.4 and 3.7), 6.11 (1 H, dd, *J* 5.6 and 2.4), 6.40 (1 H, dd, *J* 5.6 and 3.2), 7.03 (1 H, d, *J* 1.7), 7.1–7.6 (7 H, m), 7.43 (1 H, d, *J* 1.7) and 7.73 (2 H, d, *J* 8.3); **5d**: δ_H(270 MHz; $CDCl_3$; Me_4Si) 1.46 (1 H, dd, *J* 8.6, 1.6), 1.83 (1 H, d, *J* 8.6), 2.34 (3 H, s), 3.07 (1 H, br s), 3.17 (1 H, br s), 3.37 (1 H, d, *J* 5.4), 3.93 (1 H, dd, *J* 5.4 and 3.7), 6.09 (1 H, dd, *J* 5.4 and 3.1), 6.43 (1 H, dd, *J* 5.4 and 2.9), 7.05 (1 H, d, *J* 2.0) and 7.2–7.8 (10 H, m).

The stereochemistry of **5a** was established by an X-ray crystal structure analysis of a suitable crystal of **7**, which had been obtained by hydrogenation of **5a**. The stereostructure of the other *endo* adduct **5b** was confirmed by the following reaction sequence. Treatment of an original mixture of **5a–d** (**5a** enriched) with $TiCl_4$–Zn afforded a roughly 9:1 mixture of the sulfides **8** and **9** which were transformed into (±)-**5a–d** by oxidation with *m*-chloroperoxybenzoic acid. Since all isomers were separable on HPLC, in which *endo* isomers showed nearly an equal amount of **5a** and **5b**, the adduct **5b** was thus correlated with the adduct **5a** by comparison of the pertinent peak in HPLC. Isolation of pure **5c** and **5d** was difficult because of inefficient separation from each other by flash chromatography. The product ratios were determined from the integrated values of the peaks in HPLC of the mixtures.

(1*R*,2*R*,3*R*,S_S)-3′-(tolyl-*p*-sulfinyl)-2′-furoyl-3-phenylbicyclo-[2.2.1]heptane 7

A mixture of **5a** (1.80 g, 4.47 mmol) and 5% Pd on carbon (250 mg) in methanol (100 cm^3) was hydrogenated at room temperature for 2 h. The mixture was filtered with the aid of short pad of Celite and the solid filter was washed with methanol (30 cm^3). The combined washings and filtrate were concentrated under reduced pressure to afford **7** (1.75 g, 97%), mp 154 °C (recrystallised from Et_2O) (Found: C, 74.3; H, 6.0. $C_{25}H_{24}O_3S$ requires C, 74.2; H, 6.0%); $[\alpha]_D^{26}$ −467.3 (*c* 1, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3020, 2970, 1660, 1555, 1490, 1465 and 1040; δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.8–0.9 (1 H, m), 1.20–1.30 (1 H, m), 1.43–1.62 (3 H, m), 1.96 (1 H, d, *J* 9.9), 2.37 (3 H, s), 2.53 (1 H, d, *J* 4.0), 2.81 (1 H, br s), 3.47 (1 H, d, *J* 5.5), 3.64 (1 H, ddd, *J* 5.5, 4.0 and 1.5), 7.05 (1 H, d, *J* 1.8), 7.13–7.30 (7 H, m), 7.49 (1 H, d, *J* 1.8) and 7.74 (2 H, d, *J* 8.1).

Crystal data and structure determination for compound 7

Crystal data for **7**: $C_{25}H_{24}O_3S$; M = 404.52; crystal dimensions: 0.30 × 0.30 × 0.10 mm, space group: $P2_1$ (#4); V = 1073.5(2) $Å^3$; a = 8.118(1), b = 7.381(1), c = 17.965(1) Å; Z = 2; D_c = 1.251 g cm^{-3}; μ(Cu-Kα) = 15.18 cm^{-1}; R = 0.033; R_w = 0.049 for 1590 reflections [$I > 3.00\sigma(I)$].

Intensity data were collected at 298 K on a Rigaku AFC5R diffractometer with Cu-Kα radiation, λ = 1.541 78 Å. Equivalent reflections were merged and Lorentz and polarisation corrections were applied. The structure was solved by direct methods using SHELXS.[13] Atomic coordinates, thermal

† **10**: mp 97–99 °C [lit.,[10a] mp 105 °C for (±)-**10**]; $[\alpha]_D^{25}$ −94 (*c* 1, $CHCl_3$); **11**: mp 36–38 °C [lit.,[10a] mp 69–70 °C for (±)-**11**]; $[\alpha]_D^{22}$ −43.6 (*c* 0.53, EtOH) {lit.,[11c] $[\alpha]_D^{22}$ −45.9 (*c* 5.63, 95% EtOH)}; **12**: $[\alpha]_D^{25}$ −70.5 (*c* 0.5, $CHCl_3$). Judging from the high optical purity (98% ee) of **12** by chiral HPLC, the enantiomeric excess of **10** was estimated as ≥98%. A racemic sample (±)-**12** was obtained by hydrogenation of the *endo* Diels–Alder adduct[10] of methyl cinnamate and cyclopentadiene.

‡ *J* Values in Hz and $[\alpha]_D$ values in 10^{-1} deg cm^2 g^{-1}.

§ The symbol S_S expresses the absolute configuration of the sulfinyl centre as *S*.

parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/3.

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